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COMPLETE SPECIFICATION

Linear Superpolymers of Mixed Diamines

We, CALIFORNIA RESEARCH CORPORATION, a corporation duly organized under the laws of the State of Delaware, United States of America, of 200, Bush Street, San Francisco 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is directed to novel linear superpolymers of mixed meta- and para- exceptional physical properties and other advantages compared to conventional superpolymers of single diamines.

We have discovered a new class of linear superpolymers of mixed meta—and para-xylylene diamines and an aliphatic dicarboxylic acid of 6 to 10 carbon atoms in which 5 to 90 per cent, by weight, of the mixed xylylene diamines is para-xylylene diamine which possess superior physical properties over the superpolymers of meta-xylylene diamine or para-xylylene diamine alone and may be prepared more economically.

This new class of linear superpolymers is characterized by substantially higher melting points and heat distortion points compared to the superpolymers of meta-xylylene diamine alone. Synthetic fibers of these novel linear superpolymers are thus capable of withstanding to a better degree the higher temperatures encountered in the present day laundering operations of washing and ironing. The linear superpolymers of the present invention are also well suited for commercial manufacturing techniques, such as, melt spinning and extrusion unlike superpolymers of para-xylylene diamine alone. The corresponding polymers of para-xylylene diamine possess such high melting points that when they are heated decomposition or degradation, in general, sets in before they can be melted and spun or extruded.

The fact that the superpolymers of mixed meta- and para-xylylene diamines, according to the present invention, possess superior physical properties over the superpolymers of either meta-xylylene diamine or para-xylylene diamine alone is entirely unexpected. Heretofore, it has been generally recognized that superpolymers of diamines and dicarboxylic acids in which either mixed acids or mixed diamines are employed give heterogeneous compositions characterized by eutectics. These compositions are far less satisfactory for the production of synthetic fibers and films than those prepared from a single diamine and a single dicarboxylic acid. They are almost invariably affected by lower melting points, lower tensile strengths, lower crystallinity, and other less desirable physical properties. For such reasons as these, previous attempts to improve melting points and other physical characteristics of linear superpolymers by blending reactants have not been considered successful.

The only known exception, in which a superpolymer of either mixed diamines or mixed dicarboxylic acids was prepared without the formation of a eutectic mixture, was reported in an article by Edgar and Hill appearing in the Journal of Polymer Science, Volume 8, Page 1 (1952). In this article the preparation of superpolymers of mixed adipic and terephthalic acids and hexamethylene diamine which were isomorphic and gave no eutectic was described. However, when superpolymers of mixtures of adipic acid and terephthalic acid with the meta-xylylene diamine of the present compositions were prepared, it was found that a eutectic was formed contrary to expectations and that, for some nonapparent reason, the superpolymers of meta-xylylene diamine did not follow the exception noted by Edgar and Hill. In view of this behavior of meta-xylylene diamine, it was indeed surprising that the superpolymers of aliphatic dicarboxylic acid and mixed meta-xylylene diamine and para-xylylene

diamine, in accordance with this invention, were isomorphic and gave no eutectic.

In addition to their superior physical properties, the novel mixed meta- and para-xylylene diamine superpolyamides of this invention possess a decided economic advantage over the superpolymers of meta-xylylene diamine and para-xylylene diamine alone. Xylenes, which constitute an important source of raw material for the production of xylylene diamines, naturally exist in mixtures in which the para-isomer ordinarily constitutes from 25 to 30 per cent of the total meta- and para-xylenes present. The physical properties of these meta- and para-xylenes are so similar that their separation by conventional methods is extremely difficult. It follows that isolation of these isomers for the production of pure meta-xylylene diamine or para-xylylene diamine can be costly. In the present case, the naturally existing mixtures of meta- and para-xylenes may be employed as such in the production of mixed meta- and para-xylylene diamines for the superpolymers of this invention and the cost of separating the xylene mixtures is avoided.

The novel superpolyamides of our invention are prepared essentially by condensing mixed meta- and para-xylylene diamines in which up to 90 per cent, by weight, of the mixed xylylene diamines is para-xylylene diamine with an aliphatic dicarboxylic acid having an even number of 6 to 10 carbon atoms to produce a high polymer. For the most satisfactory melting points according to the most common present day manufacturing techniques, 20 to 40 per cent, by weight, of the xylylene diamine mixture is preferably para-xylylene diamine. Where higher melting point materials may be accommodated, higher ranges of 40 to 60 per cent para-xylylene diamine are particularly suitable. However, from an overall point of view, of both economics and quality, mixtures of meta- and para-xylylene diamines corresponding to the ratio of meta-para found in natural xylenes are preferred. These ordinarily contain 25 to 30 per cent, by weight, para-xylylene diamine based on total meta- and para-xylylene diamines in the mixture.

The condensation may be accomplished by heating the mixed diamines and the acid in a reaction vessel from which the water formed in the condensation reaction may be removed by distillation or other suitable means. For present purposes, a three-step procedure is preferred involving (1) forming an aqueous solution of an amine salt of the mixed meta- and para-xylylene diamines and the aliphatic dicarboxylic acid, (2) separating the amine salt or heating the aqueous solution of the amine salt to evaporate the water and form a low polymer, and (3) polymerizing the separated salt or further polymerizing the low polymer of the preceding step by heating to a high polymer.

The amine salts of the meta- and para-xylylene diamine mixtures and aliphatic dicarboxylic acid, according to this invention, are suitably prepared by neutralizing the mixed diamines in water with the aliphatic dicarboxylic acid to form an aqueous amine salt solution. Approximately equimolecular proportions of the acid and the diamine mixture are employed.

The amine salts formed in the above reaction may be precipitated and separated by several means. The aqueous solution may be cooled to a temperature at which a precipitate is formed consisting of the mixed amine salts. A lower molecular weight alcohol, such as isopropanol, may also be added to precipitate the amine salts. Following the precipitation, the amine salts may be separated by any suitable means for separating solids and liquids, such as decanting, filtering or centrifuging.

According to another method, the amine salts are not separated from their aqueous solution but the solution is heated at atmospheric pressure to remove the water and, at the same time, form an initial low polymer. This method is preferred since it avoids the use of separation equipment and facilitates the handling of materials by keeping them in liquid form.

The polymerization of the amine salt of mixed meta- and para-xylylene diamines and aliphatic dicarboxylic acid pursuant to the invention is effected by heating the salt to a temperature at which condensation occurs to form a highly polymeric product. An inert atmosphere such as nitrogen gas is desirable in this operation. After the initial formation of a low polymer, the polymerization is most conveniently continued by heating at reduced pressures of 40 millimeters of mercury or less. Temperatures in the range of 240° to 280° C. and pressures of 0.01 to 0.1 millimeters of mercury are preferred.

The mixed meta- and para-xylylene diamines may be derived from several sources. For present purposes, the mixtures were very conveniently and economically prepared by hydrogenation of a mixture of isophthalonitrile and terephthalonitrile. These mixed phthalonitriles were prepared by reacting ammonia with a mixture of iso- and terephthalic acids which, in turn, were prepared by the oxidation of mixed meta- and para-xylenes.

The aliphatic dicarboxylic acid of from 6 to 10 carbon atoms employed in the preparation of the superpolyamides of meta-xylylene diamine according to the invention are alpha- and omega-aliphatic dicarboxylic acids, that is, those having the two carboxyl groups on the ends of the carbon chain. These acids may also be described as poly-

methylene dicarboxylic acids of [illegible] to 10 carbon atoms. They may be represented by the following structural formula:

$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-OH$$

in which n is 4 to 8. Dicarboxylic acids within the above-described preferred group are adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid. Of these acids sebacic, suberic and, particularly, adipic acid are presently considered the most suitable because of the excellent crystalline characteristics and improved melting points of the mixed meta- and para-xylylene diamine superpolyamides derived from them as compared with products obtained from acids having an odd number of C atoms. For the purposes of this description, such acids are conveniently referred to as aliphatic dicarboxylic acids of an even number of 6 to 10 carbon atoms. In the above formula for acids of this type, n is an even number of 4 to 8.

In further illustration of the invention, the following examples are submitted. The proportions given, unless otherwise specified, are on a weight basis.

Example I

0.29 parts, by weight, of adipic acid, 0.5 parts, by weight, of water, and 0.54 parts, by weight, of a 50 per cent, by weight, aqueous solution of meta- and para-xylylene diamines having a meta:para weight ratio of 90:10 were placed in a glass reaction flask. An amine salt was formed by reaction of the acid and amine. The flask was fitted with an air-cooled reflux condenser, an outlet for applying a vacuum, and a gas inlet and outlet for sweeping out water formed during the reaction with nitrogen. Heat was then applied to the flask and the water was evaporated off. The heating was continued and the temperature rose to about 190° C., at which point, the salt started to polymerize. The contents of the flask were then heated to about 270° C. where a low polymer was formed. A vacuum of 0.01 to 0.1 millimeters of mercury pressure was applied and the temperature raised to about 275° C. to produce a high polymer of mixed meta- and para-xylylene diamines and adipic [illegible]

The mixed meta- and para-xylylene adipamide formed above was 10 per cent para-xylylene adipamide. It had a melting point of 245° C. and was characterized by an excellent crystalline structure. It could be melted and drawn into excellent fibers.

Example II

1.17 parts, by weight, of adipic acid were introduced into a glass reaction flask equipped with an air-cooled reflux condenser and an outlet for applying a vacuum. The flask was also provided with a gas inlet and outlet for sweeping out water formed during the reaction with nitrogen. 2.42 parts, by weight, of a 33.0 per cent, by weight, aqueous solution of meta-xylylene diamine and 0.84 parts, by weight, of a 33.0 per cent, by weight, aqueous solution of para-xylylene diamine were then added to the acid in the reaction flask. An amine salt mixture was thus formed. Heat was then applied to the flask and water was evaporated off. When the temperature rose to about 190° C., the salt started to polymerize. The temperature of the flask was then raised to 280° to 288° C., and a low polymer was formed. A vacuum of 0.01 to 0.1 millimeters of mercury pressure was applied for about 20 minutes to produce a high polymer of mixed meta- and para-xylylene diamines and adipic acid.

The mixed meta- and para-xylylene adipamide formed above was approximately 25 per cent para-xylylene adipamide. It had a melting point of 260° C. and was characterized by an excellent crystalline structure. Upon melting, the material was suitable for drawing into excellent fibers.

Additional superpolymers of various mixtures of meta- and para-xylylene diamines and aliphatic dicarboxylic acids were prepared in accordance with the procedure of the above example. Melting points of the superpolymers thus obtained are set out in Table I below.

For the purpose of comparison, an attempt was also made to prepare similar superpolymers of meta-xylylene diamine and mixed adipic and terephthalic acids. Tests on the polymers prepared in these experiments are set out in Table I.

TABLE I

Diamine	*Per Cent*	*Dicarboxylic Acid*	*Per Cent*	*Melting Point °C.*	*Remarks*
Meta-xylylene	100	Adipic	100	243	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	95 5	Adipic	100	244	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	90 10	Adipic	100	245	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	85 15	Adipic	100	249	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	75 25	Adipic	100	260	Crystalline—Melts sharply

TABLE I (*Continued*)

Diamine	*Per Cent*	*Dicarboxylic Acid*	*Per Cent*	*Melting Point °C.*	*Remarks*
Meta-xylylene Para-xylylene	65 35	Adipic	100	273	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	60 40	Adipic	100	277	Crystalline—Melts sharply
Meta-xylylene	100	Sebacic	100	193	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	95 5	Sebacic	100	197	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	90 10	Sebacic	100	200	Crystalline—Melts sharply
Meta-xylylene Para-xylylene	75 25	Sebacic	100	216	Crystalline—Melts sharply
Para-xylylene	100	Sebacic	100	300*	Partially Degraded at melting temperature
Meta-xylylene	100	Adipic	100	243	Crystalline—Melts sharply
Meta-xylylene	100	Adipic Terephthalic	95 5	238	Crystalline—Melts sharply
Meta-xylylene	100	Adipic Terephthalic	90 10	233	Crystalline—Melts sharply
Meta-xylylene	100	Adipic Terephthalic	85 15	228	Crystalline—Melts sharply
Meta-xylylene	100	Adipic Terephthalic	80 20	224	Crystalline—Melts sharply
Meta-xylylene	100	Adipic Terephthalic	70 30	228	Crystallizes poorly
Meta-xylylene	100	Adipic Terephthalic	60 40	247	Crystalline but tends to form rubbery polymer on melting
Meta-xylylene	100	Adipic Terephthalic	50 50	270	Crystalline but tends to form rubbery polymer on melting

* From the literature.

In the above table, the percentages are on a weight basis. The melting points of the polymers were taken as the temperature at which the polymer collapsed under a load in accordance with the method of Edgar and Ellery Journal of the Chemical Society, Page 2633, July 1952. From the results of the above table, it will be noted that the superpolymers of mixed meta- and para-xylylene diamines and aliphatic dicarboxylic acid, such as adipic and sebacic acid, are all characterized by improved melting points as the para-xylylene diamine content is increased. It will also be noted that these superpolymers possess a definite crystalline structure and melt sharply to produce a polymer which is excellently suited for cold drawing into fibers. By comparison, the superpolymers of meta-xylylene diamine and mixed adipic and terephthalic acids have, in general, lower melting points as the terephthalic acid content is increased. Although polymers having more than 40 per cent terephthalic acid content are higher melting than pure meta-xylylene diamine and adipic acid polymers, they tend to form rubbery polymers on melting which are generally recognized as being less suitable for the production of fibers and films.

To further illustrate the unusual physical characteristics of the mixed meta- and para-xylylene diamines and aliphatic dicarboxylic acids superpolyamides of the invention, the test results of Table I were plotted to give the accompanying drawing. As will be seen from Curves A and B of the drawing, the superpolymers of mixed meta- and para-xylylene diamines and aliphatic dicarboxylic acids give no eutectic. On the other hand, as shown by Curve C, polymers of meta-xylylene diamine and adipic acid and terephthalic acid mixtures give a definite eutectic. This renders them less suitable than pure meta-xylylene diamine and adipic acid polymer for use in the formation of fibers and films where the melting point is critical. The presence of this eutectic also demonstrates the general impracticality of improving the melting points by blending the acids.

What we claim is:—

1. A linear superpolymer of mixed meta- and para-xylylene diamines and polymethylene dicarboxylic acid of an even number of 6 to 10 carbon atoms, in which 5 to 90 per cent by weight of the mixed xylylene diamines is para-xylylene diamine.

2. A mixed meta- and para-xylylene adipamide linear superpolymer as claimed in Claim 1.

3. A mixed meta- and para-xylylene adipamide linear superpolymer as claimed in Claim 2, in which 20 to 40 per cent of the mixed xylylene adipamides is para-xylylene adipamide.

4. A mixed meta- and para-xylylene suberamide linear superpolymer as claimed in Claim 1.

5. A mixed meta- and para-xylylene sebacamide linear superpolymer as claimed in Claim 1.

6. A method of preparing linear superpolymers of mixed meta- and para-xylylene diamines and a polymethylene dicarboxylic acid of an even number of 6 to 10 carbon atoms, wherein equimolecular proportions of mixed meta- and para-xylylene diamines, in which 5 to 90 per cent by weight of the mixed xylylene diamines is para-xylylene diamine, and of a polymethylene dicarboxylic acid of an even number of 6 to 10 carbon atoms are condensed to a high polymer.

7. A method as claimed in Claim 6, wherein said acid is adipic acid, an aqueous solution of the mixed diamines being neutralised with adipic acid, and the salt thus formed being separated and heated to form a high polymer.

8. A method as claimed in Claim 7, wherein the aqueous nylon salt is heated to evaporate the water and to form a low polymer, and the low polymer is further heated to form a high polymer.

9. A method as claimed in Claim 7 or 8, wherein 20 to 40 per cent by weight of the mixed xylylene diamines is para-xylylene diamine.

10. A linear superpolymer of mixed meta- and para-xylylene diamines and an aliphatic dicarboxylic acid having an even number of 6 to 10 carbon atoms, substantially as hereinbefore described with reference to any of the specific Examples.

11. A method of preparing a linear superpolymer of mixed meta- and para-xylylene diamines and an aliphatic dicarboxylic acid, having an even number of 6 to 10 carbon atoms, substantially as hereinbefore described with reference to any of the specific Examples.

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COMPLETE SPECIFICATION
This drawing is a reproduction of the Original on a reduced scale